RELATING THEORY TO EXPERIMENT: THE OPTICAL PROPERTIES OF COPPER

A. Williams, J. Janak, V. Moruzzi

To cite this version:

A. Williams, J. Janak, V. Moruzzi. RELATING THEORY TO EXPERIMENT: THE OPTICAL PROPERTIES OF COPPER. Journal de Physique Colloques, 1972, 33 (C3), pp.C3-131-C3-134. <10.1051/jphyscol:1972319>. <jpa-00215053>

HAL Id: jpa-00215053
https://hal.archives-ouvertes.fr/jpa-00215053
Submitted on 1 Jan 1972

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
RELATING THEORY TO EXPERIMENT:
THE OPTICAL PROPERTIES OF COPPER (*)

A. R. WILLIAMS, J. F. JANAK and V. L. MORUZZI
IBM Thomas J. Watson Research Center Yorktown Heights, New York 10598

I. Introduction. — The calculation of the electronic properties of a solid involves several steps: (1) reduction of the many-electron problem to a one-electron problem characterized by an effective electron-ion potential; (2) calculation of the energy bands and wave functions implied by this potential; (3) interpolation in \( k \)-space to a mesh of points sufficiently dense to permit accurate evaluation of integrals; and (4) integration in \( k \)-space to obtain the properties of the material such as density of states, optical properties, charge densities (which form an input back into step 1 in a self-consistent calculation), etc.

We have been concerned with eliminating computational uncertainties in steps 2 through 4 so that the results accurately reflect the electron-ion potential initially used. Although such accurate calculations can be used to explain experimental results, it is equally important to bring experimental evidence to bear on the assumptions required to obtain the effective one-electron potential (and here it is crucial to ensure that no spurious features are introduced during the course of the calculation). An unambiguous estimate of the importance of many-body effects in solids, for example, is given by the difference between experiment and the results of reliable one-electron calculations.

II. Procedure. — We obtain the energy bands and interband momentum matrix elements by using the KKR method at 240 points on a simple cubic lattice in the irreducible wedge of the Brillouin zone. The energies and matrix elements on a fine mesh of 10, 100 points in the irreducible wedge are then found by using \( k \cdot p \) theory locally around each of the 240 points. Since the maximum distance over which one extrapolates in this technique is only 0.07 (\( 2 \pi/a \)), the usual problems [1] associated with \( k \cdot p \) theory are greatly reduced. Finally, integrals over the Brillouin zone are performed using the Gilat-Raubenheimer [2] method on the mesh of 10, 100 points. For a given effective one-electron potential, we currently calculate the following quantities: energy bands and momentum matrix elements (to within about 0.001 ry); density of states (\( \sim 1\% \)) and Fermi energy (obtained to four figures using a generalization of the GR method for performing volume integrals, which eliminates the necessity of numerically integrating the density of states); Fermi surface properties (de Haas-van Alphen areas and cyclotron masses) to within about 1\%, obtained using our line-integral generalization [3] of the GR method; the optical absorption \( \varepsilon_2(\omega) \) including the momentum matrix elements; and the photoemission


Fig. 1. — Fermi surface of silver.
energy distributions \( D(E, \omega) \), also obtained using our line-integral formulation. In addition, a graphics package automatically supplies computer-drawn \( E(k) \) plots, and the Fermi surface can be projected onto an oscilloscope screen (Fig. 1) and studied interactively (the user can rotate the surface, measure cross-sections, etc.). We are convinced that automated visual output will become an important part of all band calculations; it eliminates a great deal of drudgery, and, more importantly, presents masses of data in a form which can be immediately absorbed by the human mind. Features (for example, programming bugs) which are otherwise buried in huge tables of numbers can be seen at a glance.

III. Results. — A high-resolution plot of the density of states in the d-bands of palladium is shown in figure 2. Structures usually shown as peaks in such plots have been resolved here, and the van Hove singularities are apparent. The density of states, however, supplies very little information about the solid, since only one number, the density of states at the Fermi energy, is experimentally accessible (and even that number involves an electron-phonon correction).

The best source of experimental information on the ground state is the Fermi surface, particularly the cyclotron mass (which, however, also contains an electron-phonon correction) and the de Haas-van Alphen areas (which are believed to involve no many-body corrections [4]). A comparison of our theoretical results for the Chodorow potential for copper with experimental values of these quantities for certain magnetic field directions is given in Table I. The specific heat electron-phonon correction \((^\circ)\) is 1.12.

### Cyclotron Masses

<table>
<thead>
<tr>
<th>Orbit</th>
<th>( m^* ), theory</th>
<th>( m^* ), exp ((^\circ))</th>
<th>( m_{el}/m_{th} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100) belly</td>
<td>1.21</td>
<td>1.37</td>
<td>1.13</td>
</tr>
<tr>
<td>(100) rosette</td>
<td>1.22</td>
<td>1.38</td>
<td>1.13</td>
</tr>
<tr>
<td>(111) belly</td>
<td>1.25</td>
<td>1.385</td>
<td>1.11</td>
</tr>
<tr>
<td>(111) neck</td>
<td>0.402</td>
<td>0.46</td>
<td>1.14</td>
</tr>
<tr>
<td>(110) dogbone</td>
<td>1.12</td>
<td>1.29</td>
<td>1.16</td>
</tr>
<tr>
<td>(110) belly</td>
<td>1.11</td>
<td>1.225</td>
<td>1.10</td>
</tr>
</tbody>
</table>

### De Haas-van Alphen Frequencies

<table>
<thead>
<tr>
<th>Orbit</th>
<th>( f ), theory</th>
<th>( f ), exp ((^\circ))</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100) belly</td>
<td>5.95</td>
<td>6.033 7</td>
<td>1.3 %</td>
</tr>
<tr>
<td>(100) rosette</td>
<td>2.43</td>
<td>2.475 1</td>
<td>2 %</td>
</tr>
<tr>
<td>(110) dogbone</td>
<td>2.49</td>
<td>2.520 3</td>
<td>1.6 %</td>
</tr>
<tr>
<td>(111) belly</td>
<td>5.81</td>
<td>5.846 8</td>
<td>0.6 %</td>
</tr>
<tr>
<td>(111) neck</td>
<td>0.210</td>
<td>0.218 72</td>
<td>4 %</td>
</tr>
</tbody>
</table>

\(^{(\circ)}\) reference [6].
\(^{(\circ)}\) reference [7].
\(^{(\circ)}\) reference [8].

Some information about the excited states is contained in the optical absorption, \( \varepsilon_L(\omega) \). Computed and experimental [9] results for copper are shown in figure 3. The theoretical \( \varepsilon_L \) for the Chodorow potential is rather unlike the experimental result for \( \hbar \omega \sim 5 \text{ eV} \) and has about 20 % more amplitude in the peak at 5 eV. The curve shown in figure 3 was obtained by altering the d-phase shift of this potential above the Fermi energy so as to increase the \( L_1-L_2 \) gap from 4.6 to 4.9 eV. No other aspect of the calculation was adjusted. It appears, in other words, that the Chodorow potential leads to excited state energies for copper which are in error by as much as 10 %.
Still more information about the excited states is contained in the photoemission experiment, which measures a function \( D(E, \omega) \) of two variables, and thus supplies an entire surface of experimental numbers. The richness of information contained in this surface is illustrated in figure 4, which is the direct-transition theoretical result, including momentum matrix elements, following from the Chodorow potential for copper. The approximations which we use to describe the production of secondaries and transport and surface escape effects have been described elsewhere \([10]\).

but it should be pointed out here that the left-hand portions of these curves (below an initial energy of \(-5\) eV) are due entirely to secondary electrons. The approximations used to describe the secondaries in our calculations are inadequate, and these portions of the photoemission curves are in poor agreement with experiment. Let us therefore focus our attention on the primary electrons (the right-hand portions of the curves, above an initial energy of \(-5\) eV) and compare our results for certain photon frequencies to experiment \([11]\) (Fig. 5). The agreement between theory and experiment for photon energies below 16.8 eV is quite good. (The theoretical curves show somewhat sharper structure than experiment, but this simply means that our theory underestimates the lifetime broadening effects. The only scattering process considered in the calculations is pair or secondary production, and, as mentioned above, our description of this process is inadequate.) Above 16.8 eV, the theory correctly predicts trends as a function of \(\omega\): a peak appears at \(-4\) eV as \(\omega\) increases beyond 16.8 eV, and the distribution begins to narrow when \(\omega\) increases to 26.9 eV. The theory gives the correct behavior with changes in \(\omega\), but the changes occur at \(\omega\)-values which are too low. This is just what one would expect if the excited-state energies were too low; thus the photoemission data also implies that the Chodorow potential gives incorrect excited state energies, in agreement with our analysis of \(\varepsilon_2(\omega)\) for copper.

Acknowledgment. — We are indebted to A. Appel of IBM’s Computing Systems Department, whose expertise in computer graphics made figure 1 possible.
References


